

## A Photocurable Poly(dimethylsiloxane) Chemistry Designed for Soft Lithographic Molding and Printing in the Nanometer Regime

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Nanopatterning techniques that use elastomeric elements as stamps, molds, and conformable photomasks provide attractive, low-cost alternatives to photolithography and other established methods, especially for applications in areas such as plastic or molecular electronics.<sup>1</sup> The physical properties of the pattern transfer elements can limit the resolution when used in the nanometer regime. For example, tall and narrow features of surface relief are unstable to mechanical collapse when the modulus is too low.<sup>2,3</sup> They are susceptible to fracture if the physical toughness is insufficiently high. Past work in soft lithography has relied primarily on elements made with commercially available silicone elastomers that were designed for other applications. As a result, while these materials are useful, they each possess only some of the desired physical properties, which include (i) the ability to photocure (to avoid thermally induced stresses and shrinkage and to enable photopatterning), (ii) medium to high modulus (4–20 MPa represents a relevant range), with the ability to tune this property, (iii) high physical toughness (>0.1 MPa), (iv) low curing induced shrinkage (<1%), and (v) low thermal expansion coefficient (<300 ppm).

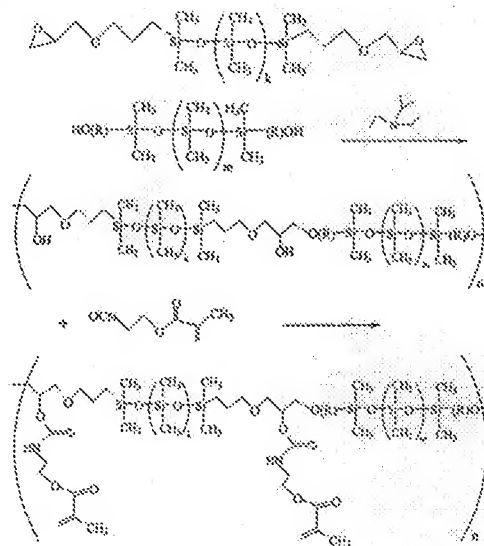
This paper introduces a modified poly(dimethylsiloxane) (PDMS) chemistry that has properties which meet many of the requirements listed above. Its structure also provides some flexibility for adjusting the material properties to match the demands of a particular patterning task. We begin by outlining the chemistry and mechanical properties of this class of material and their relationship to previously explored systems. We demonstrate its use in representative soft lithographic patterning tasks that highlight some of its attractive features.

The most widely used elastomer for soft lithography (Sylgard 184; Dow Corning) consists of a silicone “T-resin” cross-linked by a mixture of vinyl-terminated PDMS and trimethylsiloxy-terminated poly(methylhydro-siloxane) polymers. The resulting material (184-PDMS) has a highly cross-linked three-dimensional structure; it offers a high elongation at break but a relatively low modulus that can lead to structural problems in the pattern transfer elements, especially for nanometer features.

An IBM group identified a commercially available elastomer that has a relatively high compression modulus to solve the problems associated with the compliant 184-PDMS.<sup>2</sup> This material (hard-PDMS, or h-PDMS) is prepared from trimethylsiloxy-terminated vinylmethylsiloxane-dimethylsiloxane (VDT-731; Gelest) and methylhydrosiloxane-dimethylsiloxane (HMS-301; Gelest) copolymers. The h-PDMS system has cross-linkers that have relatively short lengths as compared to those in the 184-PDMS. The material has a relatively high modulus, but its elongation at break is much lower than that of 184-PDMS.<sup>2</sup> Composite bilayer patterning elements that use a thin layer of the h-PDMS with a thick backing of 184-PDMS effectively combine some of the attractive features of these two materials for certain applications.<sup>2,3</sup>

Drawbacks associated with the relatively brittle nature of the h-PDMS and the thermal curing requirements of these materials

**Scheme 1.** Preparation of a Photocurable Poly(dimethylsiloxane) Polymer for Soft Lithographic Applications in the Nanometer Regime

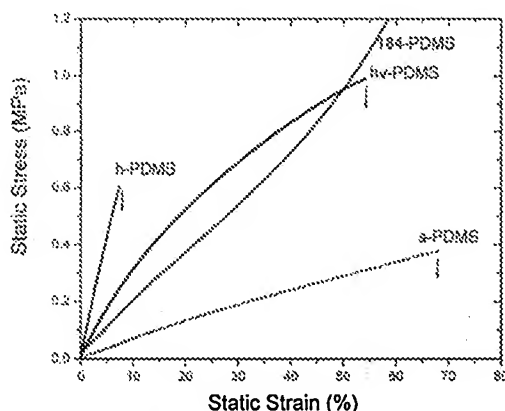


R: alkyl group

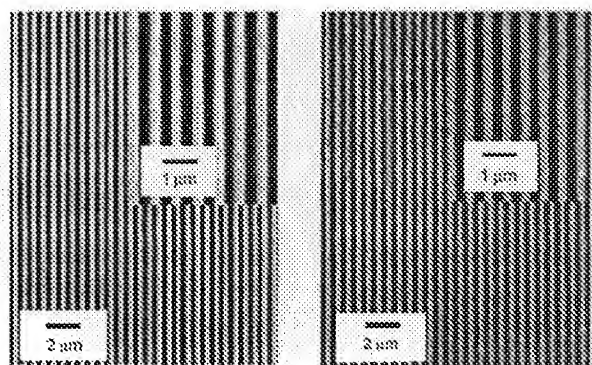
remain. A commercially available photocurable PDMS (RMS-033; Gelest) based on a (methacryloxypropyl)methylsiloxane-dimethylsiloxane copolymer avoids the latter drawback. The resulting photocured PDMS (soft-PDMS, or s-PDMS) has a modulus that is too low, however, for most soft lithographic applications, as described below.

Scheme 1 presents the synthetic procedures for preparing a new photocurable PDMS (hv-PDMS) system. The methacrylate-modified siloxane prepolymer was synthesized from diepoxide- and bis-(hydroxyalkyl)-terminated PDMS prepolymers through the “epoxy ring-opening reaction” in the presence of an amine catalyst, diisopropylethylamine. The molecular weight and the viscosity of this prepolymer were 7600–9200 (pd: 3.6 by GPC) and 118 cSt, respectively. Subsequently, the pendant hydroxyalkyl groups of the prepolymer were converted to urethane methacrylates by reaction with 2-isocyanatoethyl methacrylate. The resulting prepolymer is based on long, linear PDMS chains that are already polymerized but which remain in a viscous liquid phase. This prepolymerization minimizes the large shrinkage that can be associated with photocuring. The urethane methacrylate pendant groups serve as the rigid, photocurable cross-linkers. Their length and stiffness lie between those that are used in the 184-PDMS and h-PDMS materials.

The elastomer that results from photocuring the hv-PDMS prepolymer shows many physical properties that are attractive for soft lithography, especially for nanopatterning applications.<sup>4</sup> Mechanical measurements (Perkin-Elmer, DMA-7e) were used to determine the tensile modulus and the elongation at break of this



**Figure 1.** Static tensile stress-strain behavior of four different PDMS systems; the strain at which fracture occurs (indicated by arrows) defines the elongation at break.



**Figure 2.** SEM images of patterns on an optical adhesive (left) and the gold (right) using the new photocured hv-PDMS stamp.

**Table 1.** Comparison of Static Tensile Modulus, Elongation at Break, Physical Toughness, and Linear Polymerization Shrinkage for Different PDMS Systems

silicone elastomers	tensile modulus (MPa)	elongation at break (%)	toughness (MPa)	shrinkage (% $\pm$ 0.5%)
184-PDMS	1.8	160	4.77	1.1
h-PDMS	8.2	7	0.02	1.6
s-PDMS	0.6	70	0.13	3.1
hv-PDMS	3.4	54	0.41	0.6

material and the commercially available PDMS systems. Figure 1 and Table 1 summarize the results. These data show that the hv-PDMS provides a relatively high tensile modulus as compared to those of 184-PDMS and s-PDMS and an elongation at break that is much higher than that of h-PDMS. These properties make the hv-PDMS stamp easier to handle than the h-PDMS and less susceptible to mechanical instabilities (e.g., mechanical collapse of tall, narrow lines; see discussion of Figure 2 and refs 1 and 3) than 184-PDMS. The data also show that s-PDMS has a modulus that is much too low for most applications in soft lithography. The physical toughness (as evaluated from the area under the stress-strain curve) of hv-PDMS, while lower than 184-PDMS, exceeds that of the h- and s-PDMS.

Low shrinkage is important especially for soft lithographic applications that require multilevel pattern registration over a large area.<sup>4</sup> Shrinkage upon polymerization was measured for each material using stamps formed by casting and curing (using the

standard conditions) the corresponding prepolymers against patterns of photoresist on silicon substrates. Comparing the lateral dimensions of the relief features on these stamps to those on the "masters" reveals the dimensional changes due to curing. The hv-PDMS system has a linear polymerization shrinkage that is much lower than the commercial photocured s-PDMS, somewhat lower than h-PDMS, and slightly lower or comparable to the 184-PDMS (Table 1). hv-PDMS and 184-PDMS are based on "prepolymerized systems", which contribute to their low shrinkage.

These attractive physical characteristics have direct benefits for soft lithography. To provide an example, we demonstrated the use of hv-PDMS for a patterning task that is not well suited to the other commercial PDMS materials described here: stamping and molding with elements formed by curing against masters that have high aspect ratio, submicron features. For the case described here, the master consisted of 600 nm thick and 300 nm wide lines of photoresist, with 300 nm spaces. Our attempts to make stamps and molds out of 184-PDMS using this master failed due to mechanical feature collapse: adjacent lines in the 184-PDMS tended to merge together in an uncontrolled fashion. It is likely that the relatively low modulus of the 184-PDMS leads to this failure mode. Elements of h-PDMS showed a different problem: they tended to fail due to fracture of the relief features during fabrication of the elements or during their use, particularly in molding applications. We believe that the relatively low toughness of the h-PDMS makes relief features with these geometries susceptible to fracture.

The hv-PDMS did not exhibit these problems. Several hv-PDMS molds could be generated from a single master, and each element could be used multiple times for printing and molding. The left frame of Figure 2 shows results when the hv-PDMS is used for molding a thin film of a photocurable polyurethane (NOA 72, Norland) on a silicon wafer. The replication yields uniform, defect-free patterns over large areas ( $\sim 5$  cm<sup>2</sup>). The right frame of Figure 2 shows a pattern of a 20 nm thick layer of Au (1 nm Ti as an adhesion promoter) on a glass slide, formed using a hv-PDMS stamp and established procedures for microcontact printing. The roughness on the edges of lines is consistent with inherent limitations in the resolution of  $\mu$ CP.

In summary, this communication describes a new modified photocurable PDMS chemistry that is well suited for certain applications in soft lithography. Its physical properties are better in many respects than those of the commercially available materials that have been described in the past. In addition, the physical toughness and modulus of this material system can be adjusted by controlling the cross-linking density. Its photocurability allows the elements to be patterned by masking the exposure light. These and other possibilities will be described in future work.

**Supporting Information Available:** Experimental details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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